Time-resolved spectral imaging of LIBS plasma at low pressures for the exploration of Solar System bodies

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1. INTRODUCTION

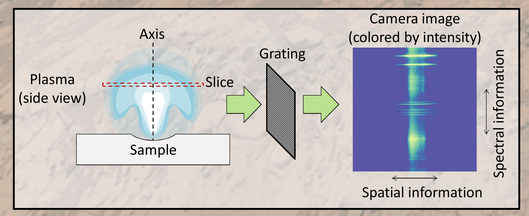
LIBS is a very useful technique for planetary exploration. ChemCam, the first LIBS instrument in space, is highly successful as part of the NASA Mars Science Laboratory [1], and will be succeeded by SuperCam on NASA's Mars 2020 mission [2], another instrument that will use LIBS to analyze Martian geology. There will also be a LIBS instrument on India's Chandrayaan-2 mission to the Moon [3], and many concepts for other missions have been proposed [4–6].

The reduced atmospheric pressure on many planetary bodies has a strong influence on the LIBS plasma: it becomes more optically thin, resulting in more material ablation, but its lifetime decreases due to expansion/cooling [7]. This tradeoff yields maximum signal intensities at 1–5 kPa, close to Martian atmospheric pressure (around 700 Pa) [8].

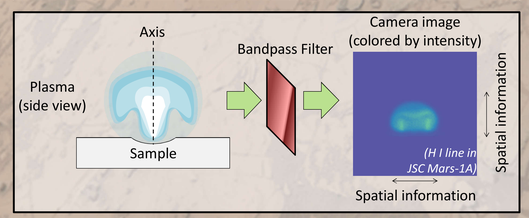
We investigate the influence of extraterrestrial atmospheric conditions with a time-resolved plasma imaging setup built around a simulation chamber. In our first results, we focus on Martian conditions. We analyze the plasma plumes of samples that are important in the context of Martian geology, like calcium sulfate, calcium fluoride, and Martian regolith simulant. We compare spatial distributions of atomic, ionic and molecular species from the atmosphere and the samples.

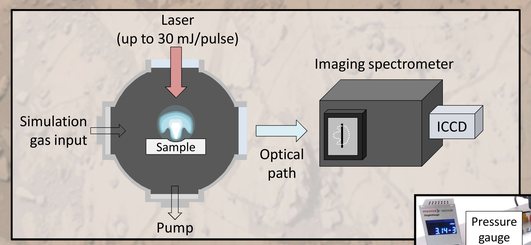
2. PLASMA IMAGING: BASICS & SETUP

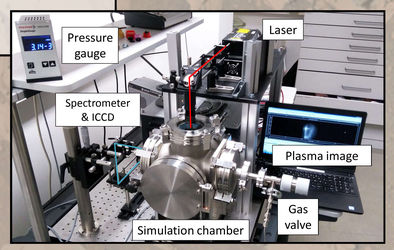
Method 1:
Measure spectrum & spatial distribution of multiple plasma slices



Method 2:
Measure spatial distribution of complete plasma at specified wavelength







Setup:

- Laser shoots vertically onto a sample in a simulation chamber
- Simulation chamber: filled with Mars simulant gas at 700 Pa pressure
- Plasma plume is imaged onto the spectrometer slit (rotated by 90°)

3. MARS CONDITIONS, OBJECTIVES, AND SAMPLES

Mars conditions:

- Atmosphere of ~95% CO_2 [9]
- Surface pressure of about 680-1100 Pa [10]

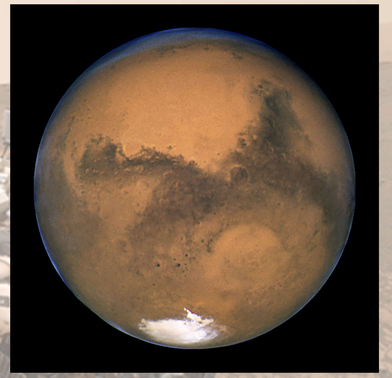
Objectives:

- Measure the spatial distributions of species from the sample (e.g. H I in hydrated samples)
- Investigate the formation of molecular bands of diatomic molecules like CaF and CaO
- Measure atmospheric signals (C I, C III, and O I), investigate their usefulness for the normalization of Martian LIBS spectra

Samples:

- Calcium sulfate ($CaSO_4 \cdot 2H_2O$)
- Sodium chloride (NaCl)
- Calcium fluoride (CaF_2)
- Martian regolith simulant JSC Mars-1A

All samples were ground into powders and pressed into pellets.



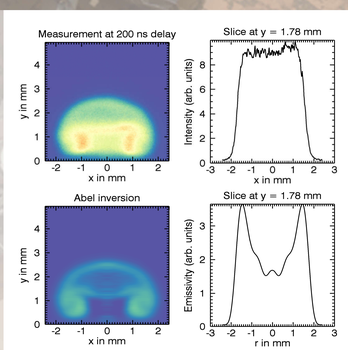
Close-up of Mars by NASA's Hubble Space Telescope.
Credit: NASA, ESA, and The Hubble Heritage Team (STScI/AURA)

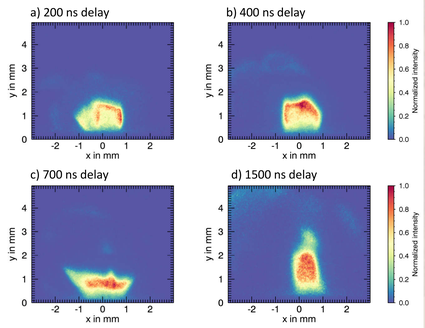
3.RESULTS

3.1. Examples of signals from the samples

Right: H I emission (656 nm) in JSC Mars-1A

- High water content of JSC Mars-1A leads to strong hydrogen signal
- Distinct shape with „whirls" at the side
  → can also be observed in calcium sulfate
  → indicates strong influence of plasma dynamics

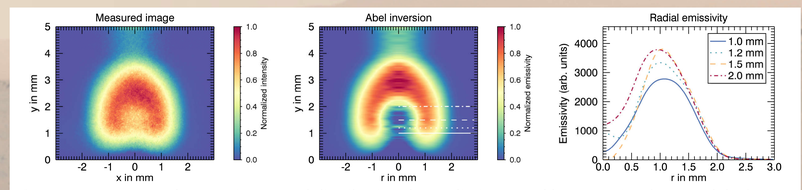




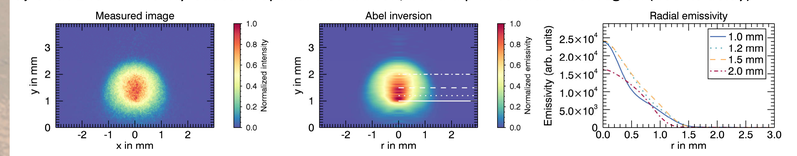
Left: CaF molecular emission (605 nm) in CaF_2 sample

- Appears after 100 ns → no long delay
- Stable intensity over a long time
  → reactions taking place over time?
- Small and located close to the center of the plasma plume
  → Surprising, as theory states that molecules should appear in low-temperature regions of the plasma
- Constantly changing shape
  → difficult to analyze

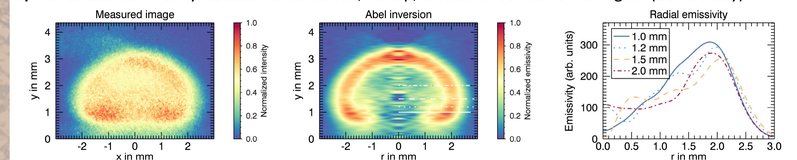
3.2. Signals from CO_2 atmosphere in calcium sulfate



a) C I at 248 nm: nearly Gaussian spatial distribution, but a dip in central lower region (100 ns delay)



b) C III at 230 nm: nearly Gaussian distribution, no dip, located in central lower region (10 ns delay)



c) O I triplet at 780 nm: dome-like distribution with low emissivity from plasma center (200 ns delay)

- C I and C III signal measured *with grating acting as bandpass filter:* grating with high number of lines (2400 l/mm), spectrometer slit open – result is image of signal where normally a peak would be
  → this method works well, but only if no other lines are close, otherwise they overlap
- C I signal surrounds C III signal → higher ionization due to higher temperature in plasma center
- Very similar results for NaCl, CaF_2, and JSC Mars-1A!
  → Overall same behavior of atmospheric signals (important for normalization!)
  → However, differences between samples exist and need to be investigated more closely
- Temperature dependence: Equation of state for uniform CO_2 atmosphere cannot explain observed spatial distributions – a gap for C II is expected, O I is expected closer to C I signal
  → assumptions not sufficient, potential effects from shockwave and plasma dynamics

CONCLUSION

Plasma imaging at simulated planetary conditions is a new and very promising technique for LIBS in planetary science. Under Martian conditions, the lack of confinement produces a large plasma with distinct inner and outer regions. This can lead to surprising results. Contrary to our initial assumption [11], molecular emission seems to be located very close to the center, even though the temperature at the center should be too high for the formation of stable molecules. This will be investigated in future studies. Atmospheric signals of C I and O I tend to be in the colder outer plasma region, as expected, but their localization cannot be fully explained by simple equilibrium models. More studies will be necessary to understand the observed distributions, how they change for different samples, and how these differences affect the feasibility of normalization of Martian LIBS spectra with signals from the CO_2 atmosphere.

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